

Final Progress Report

1. *Project Title: Investigation of Celestial Solid Analogs*

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4. *Summary*

Our far infrared studies of both hydrophobic and hydrophilic aerogel grains have demonstrated that the mm and sub-mm wave absorption produced by the fundamental two level systems (TLS) mechanism represents a more significant contribution for these open grain structures than for bulk amorphous silicate grains. We found that the region with the anomalous temperature dependence of the spectral index due to the TLS excitations can extend in a fluffy material up to 80 cm^{-1} , which is well beyond its typical upper limit for bulk glasses. Currently there is no theoretical explanation for this surprising result.

The effects of reduced dimensionality on the optical properties of carbonaceous grains have been studied with a systematic investigation of carbon aerogels. This spectroscopic approach has permitted a more reliable determination of the single grain mass normalized absorption coefficient based on the experimentally determined characteristics of the fluffy material rather than on first principles calculations involving the bulk properties of the substance. Our finding is that the electrical connectivity of the material is the main factor affecting its far infrared absorption coefficient.

Another one of the main constituents of the interstellar dust, amorphous ice, has been investigated in the mm-wave region both in the high (HDA) and low (LDA) density amorphous phases and as a function of impurities. We found that doping either phase with ionic (LiCl) or molecular (methanol) impurities decreases the difference in the mm-wave absorption coefficient between the HDA and LDA ice phases so that the HDA spectrum can be used as an analog for impure ice absorption in the far infrared spectral region.

5. *Major results*

Far infrared investigations of low dimensional effects in silica aerogel

Infrared and mm-wave radiation coming from interstellar grains located in molecular clouds, protostellar disks, and in the envelopes surrounding galactic nuclei contains important information on the geometrical structure and the orientation of the object [1], as well as providing the means for determination of the mass of the interstellar cloud [2]. Precise knowledge of optical properties of the dust is important not only for these applications, but has implications for more general star formation theories through a dramatic effect of the grain emission and absorption upon physical conditions and processes taking place within the Universe [3]. Recently from new accurate abundance determinations of stellar compositions the abundances of heavy elements were found to be only 50 – 75 % of their solar values [4]. In order to preserve the radiative properties of the dust with a smaller amount of the material J. S. Mathis suggested a modification of his previous most commonly used interstellar dust model by

assuming that the grains have a porous structure. Another development of the interstellar dust science of the last decade was the realization that the processes due to fundamental two level systems characteristic of all glasses dominate mm-wave properties of amorphous grains [5]. This brings up aerogels as a natural model of the interstellar dust materials. Combining amorphous grains and fluffy structure, the aerogel can be produced by sol gel chemical reaction and by supercritical drying from practically any astrophysically important substance. Silica aerogel consisting from nanometer size amorphous silica grains connected into a low dimension fractal structure is available both commercially and from many investigators in a broad range of densities – from under 1% of the fill fraction to more than 20%.

In our preliminary investigation of the temperature dependent mm-wave absorption of realistic laboratory analogs of the interstellar dust we tested a few samples of silica aerogel and found a surprisingly strong resonant TLS absorption in this material. This result is in a sharp contrast to the very weak effect typical for a bulk amorphous silica[6]. One of the main characteristics of the TLS resonant absorption is its high frequency spectral cutoff, which in typical glasses does not exceed 20 cm^{-1} . According to the phenomenological tunneling model of TLS [7] the width of the TLS absorption spectrum is determined by the distribution function of the tunneling parameter. Its characterization can help in the identification of the tunneling entity – the main hurdle on the road toward a microscopic theory of TLS.

In our latest series of experiments the TLS cutoff in both hydrophobic and hydrophilic silica aerogels has been measured. We made use of the anomalous temperature dependence of the resonant TLS absorption, which unlike most other far infrared absorption mechanisms decreases with increasing temperature. The surprisingly high value of the TLS cutoff parameter in the hydrophilic aerogel required several modifications in our experimental procedure. First, we had to use a second spectrometer to cover the wide spectrum range from 5 cm^{-1} to 100 cm^{-1} . Second, the standard cryostat proved to be unsuitable for this very precise cutoff measurement, and we had to construct a immersion type cryostat. A fundamental limitation to the precision of the spectral cutoff value is due to the relaxational part of the TLS absorption mechanism and it increases with temperature, compensating the resonant part of the absorption. Because of this compensating factor we were able only to show that the extent of the TLS resonant absorption in hydrophilic aerogel reaches 80 cm^{-1} , but this number may be even higher. The TLS absorption was significantly different in hydrophobic aerogel. First it was much weaker than for the hydrophilic aerogel and second, it extended only to 21 cm^{-1} , a value similar to that for the high density amorphous ice [8].

The implication of the silica aerogel experimental results for the interstellar dust models is that the TLS effects should be important over a much wider spectral range than previously thought. These results also provide a valuable clue as to the tunneling entity and its possible connection to the material dimensionality.

Far infrared absorption measurements of carbon aerogels

From our study on fluffy silicate grains we found that silica aerogel can reproduce the essential spectral properties of realistic analogues of silicate grain materials [5]. Extending the subject of the study to the carbon grains, we have measured the absorption spectra of carbon aerogel. These results provide a realistic model for carbon grains in the region $4 - 200\text{ cm}^{-1}$.

The peculiarity of carbon based materials as compared to silicates is the fact that the stable phase of carbon under normal conditions is a graphite with significant and strongly temperature dependent electrical conductivity. Reynolds *et al.* showed that carbon aerogel shows

a strong temperature dependence in the dc conductivity [9]. Furthermore, calculations and experiment show that small isolated graphitic and fullerene grains have a strong absorption feature near 2175Å similar to that found in the interstellar dust extinction [10]. The question of how well a fluffy connected material like carbon aerogel can model the extinction data is an important one.

The essential part of the calculation of the single grain mass normalized absorption coefficient from the absorption measured for the bulk material is to properly account for the local field effects. One way to do this is to determine the dielectric function of the dense material, such as graphite or amorphous carbon and calculate the single grain value, as was typically done in the past. But for a fluffy material this procedure is not very precise and can result in a very large uncertainty depending on the particular model of the fluffy grain. We chose to experimentally measure the dielectric function for the fluffy material – carbon aerogel and to calculate the single grain absorption without resorting to any connectivity model.

The single grain mass normalized absorption coefficient of carbon aerogel as a realistic analog of the fluffy carbonaceous interstellar dust material was found to be $\sim 9 \text{ cm}^2/\text{g}$ at 10 cm^{-1} , significantly less than $66 \text{ cm}^2/\text{g}$, recently published for other proposed carbon grain analogs, but close to the values typically used in the calculations based on the graphite characteristics of the grains. The resulting value for the single grain mass normalized absorption coefficient is similar to that found for various coal samples which all had coefficients of about $10 \text{ cm}^2/\text{g}$ or less.

Our carbon aerogel mm-wave absorption measurements confirm that the single grain mass normalized absorption coefficient is more or less uniform and is dominated by the graphitic component of the grain while the different connectivity of the bulk results in materials with very different spectral properties.

Influence of impurities on the mm-wave absorption in amorphous ice

Both high density and low density amorphous ices can be found in the frost on interstellar grains depending on the environment and formation conditions [11]. Since astrophysical ices are expected to be impure, this work investigates the effect of two different kinds of impurities (ionic and molecular) on the mm-wave spectral properties of the two amorphous ice phases. In 1984, Mishima et al. established [12] that high density amorphous (HDA) ice can be produced in the laboratory by compression of regular ice at 1 GPa and 77 K. At $\sim 120 \text{ K}$ and atmospheric pressure the HDA phase transforms into the low density amorphous (LDA) phase, which in turn transforms into crystalline cubic ice at $\sim 150 \text{ K}$ and finally into regular hexagonal ice at 225 K . The temperature dependant mm-wave absorption of HDA ice is typical of amorphous solids and is dominated by a broad distribution of two level systems (TLS) at low temperatures. The TLS absorption coefficient has a unique temperature dependent signature in that it becomes weaker with increasing temperature up to about 15 K . At higher temperatures the absorption coefficient again increases due to a phonon-assisted tunneling relaxational mechanism. Such changes in the absorption coefficient of high density and low density amorphous ices produces temperature dependent spectral indices [5].

The spectroscopic samples of the HDA ice are produced by compressing regular ice I_h at liquid nitrogen temperature to $1.66 \pm 0.2 \text{ GPa}$. The regular ice is made from HPLC grade water, degassed by triple freezing-thawing procedure and held in indium open-ended cups. These are placed in a 10 mm die set. The entire assembly is then immersed in liquid nitrogen. To prevent the ice from sticking to the anvils both are covered with a $6 \mu\text{m}$ Teflon film. The thickness of the resulting amorphous ice cylinders used in these experiments varied from 0.4 mm to 15 mm. The

samples are removed at atmospheric pressure while still at 77 K, mounted in the sample holder while still under liquid nitrogen and the assembly is then inserted into a precooled transmission light pipe - detector cryostat. Temperature dependent transmission spectra in the spectral region 2 - 30 cm^{-1} are measured with a lamellar Fourier transform spectrometer together with a germanium bolometer which operates at 0.3 K [5]. At the conclusion of these measurements, heating the samples to 145 K and cooling back down to low temperatures prepares the LDA phase. Impurities of methanol (molecular type) in the range 1 to 7 mol%, of LiCl (ionic type) in the range 0.5 to 5 mol%, and of 5 wt% of charcoal (carbon type) were used in the present work.

The high-density amorphous (HDA) phase has a large mm-wave absorption coefficient with strong temperature dependence, whereas the low-density amorphous (LDA) phase has an absorption coefficient smaller by a factor of 5, and it is practically temperature independent [8].

The LiCl impurity-induced contribution to the absorption coefficient for the HDA and LDA phases has been measured [8]. At 1.3 K the mm-wave absorption grows in strength with increasing LiCl content in the HDA ice, while for the LDA phase it first decreases and then increases for concentrations higher than 1.5 mol%. With increasing methanol concentration the low temperature HDA ice absorption coefficient again increases. For the LDA phase it first decreases and then increases for concentrations higher than 3 mol%. It is proposed that due to phase segregation during freezing, the concentration of impurities is spatially inhomogeneous and that this spatial inhomogeneity is probably responsible for the unusual concentration dependence of the absorption coefficient in the doped LDA ice.

These low temperature absorption coefficient data can be characterized by a simple power law with two parameters, namely,

$$\alpha = \alpha_0 (\omega / 10 \text{cm}^{-1})^\beta \quad (1)$$

where α_0 is the absorption coefficient at 10cm^{-1} , ω is the frequency in wavenumbers ($1/\lambda$), and β is the spectral index. The power law fit to the absorption coefficient minimum of α_0 coincides with the maximum of the spectral index β , both for methanol and LiCl impurities. The β maximum approaches the pure HDA ice value of 2.9 ± 0.1 , suggesting that scattering due to the non-uniformities is minimal for that concentration

Temperature jump measurements can be used to identify the TLS induced change of the absorption coefficient. There is no dramatic influence by the impurities on the temperature dependent part of the mm-wave absorption for HDA phase although the TLS effect is slightly reduced for methanol. The temperature jump measurements give very different results for the doped LDA ices. For an ionic type dopant (LiCl) the temperature dependent TLS absorption effect is increased several times, while for a molecular dopant (methanol) the size of the change is much more modest. The important find is that both dopants reduce the differences between the temperature dependent properties of the HDA and LDA ices.

The general finding of our study is that the doping with ionic (LiCl) or molecular (methanol) impurities does not alter the temperature dependence of the absorption coefficient in the HDA phase, but greatly increases its value in the LDA phase. The temperature dependent absorption coefficient increases between 4 and 11 times for methanol and between 4 and 24 times for LiCl for these concentrations in comparison to the pure LDA ice. Since these impurities decrease the difference in the mm-wave absorption coefficient between the HDA and LDA ice phases we conclude that the HDA spectrum can be used to model the mm-wave absorption properties of impure amorphous ice.

6. References

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